

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problems Mailbox.**

⑯

EUROPEAN PATENT APPLICATION

⑯ Application number: 86304692.6

⑯ Int. Cl.: C 08 F 4/68, C 08 F 10/00

⑯ Date of filing: 18.06.86

⑯ Priority: 18.06.85 JP 130885/85

⑯ Applicant: TOA NENRYO KOGYO KABUSHIKI KAISHA,
1-1 Hitotsubashi, 1-Chome Chiyoda-Ku, Tokyo 100 (JP)

⑯ Date of publication of application: 30.12.86
Bulletin 86/52

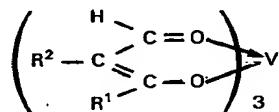
⑯ Inventor: Suzuki, Shigeo, 509-7, Minowa-cho Kohoku-ku,
Yokohama-shi Kanagawa-ken (JP)
Inventor: Doi, Yoshiharu, 2617-39, Imajuku-cho Asahi-ku,
Yokohama-shi Kanagawa-ken (JP)
Inventor: Soga, Kazuo, 30-2, Enokigaoka Midori-ku,
Yokohama-shi Kanagawa-ken (JP)

⑯ Designated Contracting States: BE DE FR GB IT NL SE

⑯ Representative: Northover, Robert Frank et al, ESSO
Chemical Limited Esso Chemical Research Centre P.O.
Box 1, Abingdon Oxfordshire, OX13 6BB (GB)

⑯ Catalyst for polymerization of olefins.

⑯ A catalyst for polymerization of olefins which comprises a
vanadium compound of the formula:



⑯ (where R¹ is an alkyl group or aryl group having 1 to 8 carbon atoms; and R² is an alkyl group or aryl group having from 1 to 8 carbon atoms, or hydrogen)
and the organoaluminum compound of the formula R₂AlX
(where R is a hydrocarbon group having 1 to 8 carbon atoms,
and X is a halogen atom).

EP 0 206 753 A1

1 CATALYST FOR POLYMERIZATION OF OLEFINS

2

3 The present invention relates to a catalyst for the living poly-
4 merization of olefins such as propylene.

5

6 The present inventors had previously found that the living poly-
7 merization proceeds to give a nearly monodisperse polymer when pro-
8 pylene is polymerized using a catalyst composed of V(acetylacet-
9 tonate)₃ and Al(C₂H₅)₂Cl. [Macromolecules, 12, 814 (1979)]

10 This catalyst, however, has a disadvantage of being poor in poly-
11 merization activity, because only several percent of vanadium in the
12 catalyst forms the active site for polymerization and the growth
13 reaction of polymer chain is slow.

14 Problems to be solved by the invention

15 Object of the invention

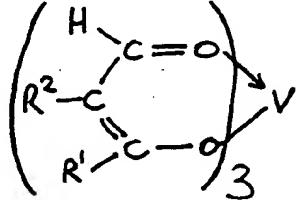
16 It is an object of the present invention to provide a vanadium-
17 based catalyst for the polymerization of olefins which has a high
18 polymerization activity per unit amount of vanadium.

19 Means to solve the problems

20 Summary of the invention

21 The present inventors found that the object of the invention is
22 achieved by using as a catalyst component a vanadium compound in
23 which β -ketoaldehyde is a chelate in place of the previous vanadium
24 compound in which β -diketone is a chelate. The present invention was
25 completed on the basis of this finding.

26 Accordingly, the gist of this invention resides in a catalyst for
27 polymerization of olefins which comprises a vanadium compound of the
28 formula:

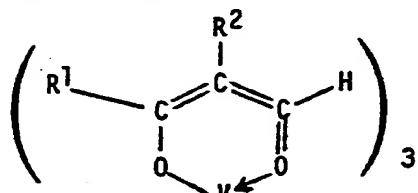


29 (where R¹ is an alkyl group or aryl group having 1 to 8 carbon
30 atoms; and R² is an alkyl group or aryl group having 1 to 8 carbon
31 atoms, or hydrogen) and an organoaluminum compound, ~~and~~ preferably of

1 the formula R_2AlX (where R is a hydrocarbon group having 1 to 8
2 carbon atoms, and X is a halogen atom).

3 Polymerization catalyst

4 The polymerization catalyst of this invention is composed of a
5 β -ketoaldehyde vanadium chelate (referred to as the vanadium compound
6 hereinafter) of the formula below:



7 (where R^1 and R^2 are defined as above) and an aluminum compound
8 of the formula R_2AlX (where R and X are defined as above).

9 Illustrative, but non-limiting, examples of the vanadium compound
10 include $V(3\text{-oxobutanalate})_3$, $V(2\text{-methyl-3-oxobutanalate})_3$, $V(2\text{-ethyl-3-oxopentanalate})_3$, and $V(2\text{-phenyl-3-oxobutanalate})_3$.

12 Illustrative, but non-limiting, examples of the aluminum compound
13 include dimethyl aluminum chloride, diethyl aluminum chloride,
14 diethyl aluminum bromide, and diisobutyl aluminum chloride.

15 The polymerization catalyst of this invention is used for the
16 living polymerization of olefins and preferably propylene.

17 Living polymerization of olefins

18 The living polymerization is performed by homopolymerizing one or
19 more olefins and preferably propylene or copolymerizing propylene
20 with other olefins in the presence of the polymerization catalyst of
21 the invention.

22 Examples of the olefin include ethylene, and alpha-olefins such
23 as 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene. The poly-
24 merization catalyst of this invention is especially useful for the
25 homopolymerization of propylene and the copolymerization of propylene
26 with ethylene or an alpha-olefin other than propylene (referred to as
27 the comonomer hereinafter).

28 The copolymerization of propylene with a comonomer is accom-
29 plished by random copolymerization of propylene and comonomer, block
30 copolymerization of propylene homopolymer and comonomer, or block
31 copolymerization of a propylene-comonomer random copolymer and
32 comonomer.

1 The polymerization reaction should preferably be carried out in a
2 solvent which is inert to the polymerization reaction and is liquid
3 at the time of polymerization. Examples of the solvent include
4 saturated aliphatic hydrocarbons such as propane, butane, pentane,
5 hexane, and heptane; saturated alicyclic hydrocarbons such as cyclo-
6 propane and cyclohexane; and aromatic hydrocarbons such as benzene,
7 toluene, and xylene.

8 The homopolymerization of propylene or the random copolymeriza-
9 tion of propylene with a comonomer should preferably be accomplished
10 by adding in succession a solution of the aluminum compound and a
11 solution of the vanadium compound to a solution of propylene or a
12 solution of propylene and comonomer dissolved in a solvent.

13 In the homopolymerization of propylene or the random copolymeri-
14 zation of propylene with comonomer, the polymerization catalyst is
15 used in such an amount that the vanadium compound is 1×10^{-6} to
16 0.01 mol , preferably 5×10^{-5} to $5 \times 10^{-3} \text{ mol}$, and the organo-
17 aluminum compound is 1×10^{-4} to 0.1 mol , preferably 5×10^{-3} to
18 0.01 mol , for 1 mol of propylene or 1 mol of propylene and comonomer
19 in combination. In addition, the amount of the organoaluminum com-
20 pound should be 10 to 1000 mol for 1 mol of the vanadium compound.

21 The molecular weight and yield of the living propylene homo-
22 polymer or the living propylene random copolymer may be properly
23 adjusted by changing the reaction temperature and reaction time. If
24 the polymerization temperature is low, particularly below -60°C , the
25 resulting polymer has a molecular weight distribution which is close
26 to that of monodisperse polymer. Polymerization at -65°C or below
27 affords a living polymer having an \bar{M}_w/\bar{M}_n of 1.05 to 1.50 (where \bar{M}_w is
28 the weight-average molecular weight and \bar{M}_n is the number-average
29 molecular weight).

30 The polymerization reaction permits the use of a reaction
31 accelerator such as anisole, water, alcohols (methanol, ethanol, iso-
32 propanol, etc.), and esters (ethyl benzoate, ethyl acetate, etc.).
33 The reaction accelerator is used usually in an amount of 0.1 to 2 mol
34 for 1 mol of the vanadium compound.

35 The comonomer in the living random copolymer of propylene and
36 comonomer usually accounts for up to 80 wt%. This amount can be
37 adjusted by changing the amount of comonomer used at the time of
38 living polymerization. When the amount of comonomer, especially

1 ethylene, is increased, the resulting copolymer has a broad molecular
2 weight distribution. Where a living copolymer of high ethylene con-
3 tent with a narrow molecular weight distribution is to be produced,
4 polymerization should preferably be performed in the following
5 manner. That is, living polymerization for a very small amount of
6 propylene should be performed before living copolymerization for pro-
7 pylene and ethylene. This permits the introduction of a large amount
8 of ethylene into the copolymer, while keeping the molecular weight
9 distribution of the living copolymer narrow. This polymerization
10 method is illustrated with an example below. At first, propylene
11 alone is supplied to the polymerization system to produce living
12 polypropylene having a number-average molecular weight of preferably
13 500 to 2,000. Then, ethylene is supplied in the presence of a large
14 amount of unreacted propylene monomer to continue living polymeri-
15 zation until the random copolymerization of ethylene and propylene
16 comes to an end.

17 The thus obtained living homopolymer of propylene or living ran-
18 dom copolymer of propylene and comonomer is made into a living block
19 copolymer by living polymerization with a comonomer. This is accom-
20 plished by supplying a comonomer (which is different from the one
21 used in the living random copolymerization with propylene) to the
22 system in which the living homopolymer or living random copolymer and
23 propylene are present, and performing living polymerization in the
24 same manner as mentioned above. Usually, the comonomer accounts for
25 up to 50 wt% in the block portion of the block copolymer. This
26 amount can be adjusted by changing the amount of the comonomer used
27 at the time of block copolymerization.

28 According to the above-mentioned method, it is possible to pro-
29 duce a living propylene polymer having a number-average molecular
30 weight (in terms of propylene [to be repeated hereinafter]) of about
31 500 to about 1,000,000 which is similar to that of monodisperse
32 polymers.

33 Effect of the invention

34 The polymerization catalyst of this invention, when used for
35 living polymerization of propylene, exhibits ten times to several
36 tens times higher polymerization activity than the conventional
37 $V(\text{acetylacetone})_3$ catalyst.

1 Examples

2 The invention is described in more detail with reference to the
3 following examples. The following methods were applied to
4 characterize the resulting polymers.

5 Molecular weight and molecular weight distribution: Measured by
6 the use of GPC (gel permeation chromatography), Model 150, made by
7 Waters Co., Ltd. The solvent was trichlorobenzene. Measuring con-
8 ditions: 135°C, solvent flow rate = 1.0 ml/min, and sample concen-
9 tration = 0.15 wt/vol%. The column was GMH6 made by Toyo Soda Mfg.
10 Co., Ltd. A calibration curve for polystyrene was made for the stan-
11 dard sample of monodisperse polystyrene available from Waters Co.,
12 Ltd. On the basis of this calibration curve, a calibration curve for
13 the polypropylene was made according to the universal method.

14 Stereoregularity of polymer: Determined by means of ^{13}C NMR
15 analysis. Model XL-200 with PFT (pulse Fourier transform unit), made
16 by Varian Co., Ltd. Conditions: 50 MHz, 120°C, pulse width 8.2 μs
17 $\pi/3$, pulse interval 4 seconds, and integration 5000 times. The
18 sample was dissolved in a 2:1 mixed solvent of trichlorobenzene and
19 heavy benzene.

20 Example 1

21 In a 200 ml autoclave, with atmosphere therein completely
22 replaced with nitrogen gas, was placed toluene as a solvent, followed
23 by cooling to -70°C. At this temperature, 35 g (0.83 mol) of pro-
24 pylene was added and dissolved in the toluene. Then, 20 mmol of
25 $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ dissolved in toluene and 0.05 mmol of $\text{V}(\text{2-methyl}-$
26 3-oxobutanalate)₃ dissolved in toluene were added to start polymer-
27 ization at -70°C. Three hours later, the reaction solution was
28 poured into cooled ethanol (-78°C) to precipitate the polymer. The
29 resulting polymer was washed five times with 500 ml of ethanol,
30 followed by drying. The polymer (0.78 g) thus obtained was found to
31 have a molecular weight and molecular weight distribution of $\bar{M}_n =$
32 17,000 and $\bar{M}_w/\bar{M}_n = 1.3$, respectively. It was a nearly mono- disperse
33 polymer.

34 The examination of the resulting polymer for stereoregularity
35 indicated that the syndiotactic fraction was 0.79, which is almost
36 equal to that of polymers obtained with the conventional $\text{V}(\text{acetyl}-$
37 acetonate)₃.

1 Comparative Example 1

2 The polymerization of propylene was performed in the same manner
3 as in Example 1, except that the $V(2\text{-methyl-3-oxobutanalate})_3$ was
4 replaced by $V(\text{acetylacetone})_3$. The yield of the polymer was
5 0.08 g, $\bar{M}_n = 30,000$, and $\bar{M}_w/\bar{M}_n = 1.2$.

6 Examples 2 to 6

7 The polymerization of propylene was performed in the same manner
8 as in Example 1, except that the polymerization time and the amount
9 of polymerization catalyst were changed as shown in Table 1 and the
10 polymerization temperature was changed to -78°C . The results are
11 shown in Table 1.

Table 1

Example	Polymer- ization time (h)	Catalyst		Yield (g)	\bar{M}_n	\bar{M}_w/\bar{M}_n
		Al (mmol)	V (mmol)			
2	3	5.0	0.5	0.21	6,700	1.3
3	6	5.0	0.5	3.07	73,000	1.3
4	32	5.0	0.05	0.70	13,000	1.2
5	6	20.0	0.1	0.42	17,000	1.2
6	6	5.0	0.1	0.14	9,800	1.5

12 Example 7

13 The polymerization of propylene was performed in the same manner
14 as in Example 5, except that 0.05 mmol of anisol was added to the
15 polymerization system. The yield of the polymer was 0.58 g, $\bar{M}_n =$
16 17,000, and $\bar{M}_w/\bar{M}_n = 1.2$.

17 Example 8

18 The polymerization of propylene was performed in the same manner
19 as in Example 6, except that 0.05 mmol of water was added to the
20 polymerization system. There was obtained 0.24 g of polypropylene
21 having $\bar{M}_n = 15,000$ and $\bar{M}_w/\bar{M}_n = 1.3$.

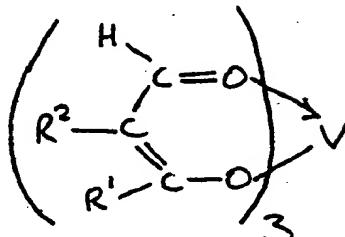
22 Example 9

23 The polymerization of propylene was performed for 22 hours in the
24 same manner as in Example 6, except that $V(3\text{-oxobutanalate})_3$ was
25 used as the vanadium compound. There was obtained 1.4 g of polypro-
26 pylene having $\bar{M}_n = 71,000$ and $\bar{M}_w/\bar{M}_n = 1.3$.

CLAIMS:

1. A catalyst system comprising a vanadium chelate of a beta-ketoaldehyde and an organoaluminum compound.

2. The catalyst system of claim 1 wherein the vanadium chelate is of the formula:



wherein R^1 is an alkyl or aryl group having 1 to 8 carbon atoms and R^2 is an alkyl or aryl group having from 1 to 8 carbon atoms or hydrogen and the organoaluminum compound is represented by the formula R_2AlX wherein R is a hydrocarbyl group having from 1 to 8 carbon atoms and X is a halogen.

3. The catalyst system of claim 2 wherein the vanadium chelate is one of $V(2\text{-methyl-3-oxobutanalate})_3$, $V(3\text{-oxobutanalate})_3$, $V(2\text{-ethyl-3-oxopentanalate})_3$ and $V(2\text{-phenyl-3-oxobutanalate})_3$.

4. The catalyst system in accordance with claim 2 wherein the organoaluminum compound is one of dimethyl aluminum chloride, diethyl aluminum chloride, diethyl aluminum bromide and diisobutyl aluminum chloride.

5. The catalyst system of claim 2 wherein the range of organoaluminum compound to vanadium chelate is in the range of 10-1,000:1 on a mol basis.

6. A living polymerization process comprising polymerizing one or more olefins in the presence of a catalyst system as claimed in any of claims 1 to 5.



European Patent
Office

0206753

Application number

EP 86 30 4692

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P, X	MAKROMOLEKULARE CHEMIE, RAPID COMMUNICATIONS, vol. 6, no. 10, October 1985, pages 639-642, Basel, CH; Y. DOI et al.: "A perfect initiator for "living" coordination polymerization of propene: tris(2-methyl-1,3-butanedionato)v anadium/diethylaluminium chloride system" * Whole document *	1-6	C 08 F 4/68 C 08 F 10/00
D, A	MAKROMOLEKULARE CHEMIE, vol. 180, 1979, pages 1359-1361; Y. DOI et al.: "Preparation of "living" polypropylenes by a soluble vanadium-based Ziegler catalyst" * Whole document *	1	
A	US-A-3 349 064 (A. GUMBOLDT et al.) * Claims; column 2, lines 22-47 *	1	C 08 F
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
Place of search	Date of completion of the search	Examiner	
THE HAGUE	19-09-1986	DE ROECK R.G.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			